

# Trends in Bulk Compressibility of $\text{Mo}_{2-x}\text{W}_x\text{BC}$ Solid Solutions

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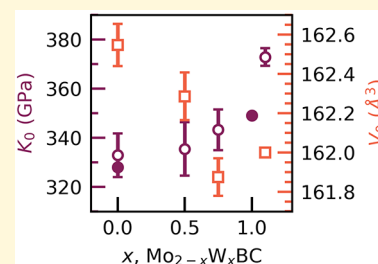


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**ABSTRACT:** The  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  system is of interest as a material with high hardness while maintaining moderate ductility. In this work, synchrotron diffraction experiments are performed on  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions, where  $x = 0, 0.5$ , and  $0.75$ , upon hydrostatic compression to  $\sim 54$  GPa,  $\sim 55$  GPa, and  $\sim 60$  GPa, respectively. Trends in bulk modulus,  $K_0$ , are evaluated by fitting collected pressure–volume data with a third-order Birch–Murnaghan equation of state, finding  $K_0 = 333(9)$  GPa for  $\text{Mo}_2\text{BC}$ ,  $K_0 = 335(11)$  GPa for  $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$ , and  $K_0 = 343(8)$  GPa for  $\text{Mo}_{1.25}\text{W}_{0.75}\text{BC}$ . While  $K_0$  seems to express a slight increase when Mo is substituted by W, calculated zero-pressure unit cell volume,  $V_0$ , exhibits the opposite trend. The decrease in  $V_0$  corresponds to an increase in valence electron density, hardness, and  $K_0$ . Observations align with previously reported computational results and will inform future efforts to design sustainable materials with exceptional mechanical properties.



## INTRODUCTION

The automotive, aerospace, defense, and health care industries, among others, depend on materials with enhanced hardness.<sup>1</sup> Efforts to discover superhard materials, with a Vickers hardness ( $H_V$ )  $\geq 40$  GPa, have largely relied upon simple design rules and trial-and-error approaches.<sup>2</sup> Accordingly, attempts to mimic the structural and mechanical properties of diamond ( $H_V \approx 90$ – $100$  GPa), the prototypical superhard material, have manipulated light, main group elements to achieve the desired strong, dense 3D network of short covalent bonds.<sup>3–6</sup> Cubic boron nitride ( $c\text{-BN}$ ,  $H_V = 55$  GPa) and  $\text{BC}_2\text{N}$  ( $H_V = 65$  GPa) are examples of this type.<sup>7–9</sup> However, the synthesis of diamond and other hard materials in its class is often cost-prohibitive, requiring extreme temperatures and pressures.<sup>2</sup> To combat the exorbitant synthetic costs, researchers have directed focus toward another class of hard materials: transition metal (TM) borides such as  $\text{ReB}_2$  ( $H_V = 45$  GPa) and  $\text{WB}_4$  ( $H_V = 43$  GPa).<sup>10–12</sup> Integration of the TMs simplifies material synthesis because conventional arc melting processes can yield the desired structures. In these structures, the light boron atoms support the formation of covalent bonding networks, while the heavy TMs are intrinsically incompressible due to their high valence electron density, properties well understood to promote hardness.<sup>1,3,12–14</sup>

Incorporating TMs into superhard materials discovery efforts unearths a vast, underexplored compositional space and provides an excellent opportunity to investigate new materials compositions with optimized mechanical properties. Although superhard materials of this type are often impractical as candidates for industrial use as the TMs employed can be expensive and scarce, sustainability concerns can be addressed through elemental substitution of the expensive, rare-earth TMs with more earth-abundant metals.<sup>2</sup> TM substitution can

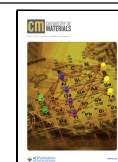
also modify valence electron concentration (VEC) and atomic size effects to tailor mechanical properties. For instance, substitution of W with Ti, Zr, Hf, Mo, Ta, Mn, or Cr improves hardness of  $\text{WB}_4$ -based solid solutions from  $H_V = 43$  GPa to greater than  $H_V = 50$  GPa.<sup>15–17</sup> Similarly,  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$  demonstrates improved hardness compared to its isostructural parent composition,  $\text{Mo}_2\text{BC}$ , with  $H_V = 42.1$  GPa and  $H_V = 26.5$  GPa, respectively, at  $0.49$  N indentation load.<sup>18</sup>

The  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solution system is of particular interest because it provides the unique opportunity to optimize hardness while maintaining moderate ductility, contradictory extrinsic properties often challenging to predict and control. Although hardness and ductility are difficult to predict directly, bulk modulus ( $K$ ) and shear modulus ( $G$ ) are intrinsic material properties that correlate to ductility, brittleness, and hardness, allowing for indirect estimations. Pugh's ratio,  $G/K$ , estimates ductility in inorganic compounds, as compounds with  $G/K < 0.57$  are considered ductile and those  $\geq 0.57$  brittle.<sup>19</sup> The elastic moduli of hard, isostructural  $\text{MoWBC}$  and  $\text{Mo}_2\text{BC}$  have been investigated using density functional perturbation theory, finding  $G/K = 0.579$  and  $0.576$ , respectively.<sup>18</sup> Thus, it is suggested that ductility is preserved in the  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  system regardless of the TM ratio, even though elemental substitution of Mo with W results in increased hardness. A separate *ab initio* study of  $\text{Mo}_2\text{BC}$  also suggests moderate ductility due to the presence of both the metallic interlayer bonding and stiff

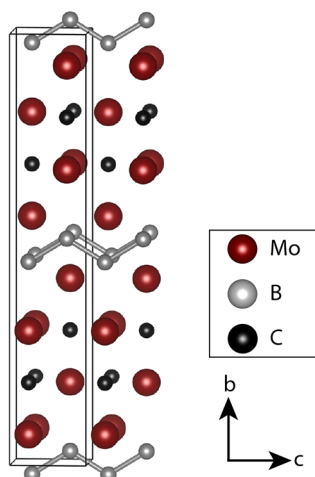
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carbide and boride layers.<sup>20</sup> While ductility is uncommon in hard materials, so is anisotropy due to the orientation-dependent mechanical response. Examining the  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  ( $0 \leq x \leq 1.1$ ) crystal structure, the unit cell is highly anisotropic, crystallizing in an orthorhombic space group ( $Cmcm$ ) isostructural to the  $\text{Mo}_2\text{BC}$  parent phase, visualized in Figure 1. Boron atoms are bound together in chains extending



**Figure 1.** Crystal structure of  $\text{Mo}_2\text{BC}$ , isostructural to  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions when  $0 \leq x \leq 1.1$ . Visualized using VESTA software.<sup>22</sup>

in the  $[001]$  direction, while the two crystallographically independent  $TM$  sites (Wyckoff  $4c$ ) are occupied by a statistical mixing of Mo and W. The ability to maintain ductility in high-hardness materials is an intriguing concept as conventional superhard materials are typically brittle (i.e., diamond  $G/K = 1.21$ ).<sup>21</sup>

Experimental determination of trends in  $K$  within  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions is a pragmatic step toward informing computational efforts and developing an improved understanding of the balance between elastic moduli, hardness, and ductility in  $TM$ -based hard, incompressible materials. Bulk compressibility can be determined through *in situ* hydrostatic compression experiments in the diamond anvil cell (DAC). In this process, synchrotron diffraction patterns are incrementally collected upon compression, monitoring changes in lattice parameters and fitting an equation-of-state (EOS) to the resultant relative cell volume versus pressure curves. DAC experiments on the tungsten-rich composition,  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$ , revealed its ultraincompressibility with  $K = 373$  GPa.<sup>23</sup> This work investigates trends in hydrostatic compressibility of other  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions, where  $x = 0, 0.5$ , and  $0.75$ , to elucidate correlations among composition manipulation and physical and mechanical properties of  $TM$ -based, hard, incompressible materials. Results will inform future materials design efforts in the quest to optimize mechanical properties while considering synthetic accessibility and material sustainability, providing significant opportunity for applications requiring wear-resistant, superhard materials.

## EXPERIMENTAL METHODS

Three isostructural  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  compositions, where  $x = 0, 0.5$ , and  $0.75$ , were synthesized as in a previous work.<sup>18</sup> Stoichiometric ratios of the starting materials, including Mo (Alfa Aesar, 99.95%), W (Alfa Aesar, 99.5%), crystalline B (Alfa Aesar, 99.5%), and graphite (Sigma-Aldrich, 99.99%), were weighed out to a total mass of 0.25 g and pressed into 6 mm pellets. The pellets were arc melted in a flowing argon atmosphere on a water-cooled copper hearth, flipping each sample at least twice to ensure homogeneous melting and thorough mixing of the elements.

To evaluate bulk compressibility, synchrotron diffraction experiments were performed on each  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  composition under compression. A Diamonite mortar and pestle was used to grind the

**Table 1.** Refined Lattice Parameters for  $\text{Mo}_2\text{BC}$  and the Associated Pt Pressure Calibrant with Calculated Pressure Values

| $\text{Mo}_2\text{BC}$ |            |            | Pt         |           |           |
|------------------------|------------|------------|------------|-----------|-----------|
| $R_{wp}^a$             | $a$ (Å)    | $b$ (Å)    | $c$ (Å)    | $a$ (Å)   | $P$ (GPa) |
| 1.60                   | 3.0803(1)  | 17.3113(6) | 3.03997(8) | 3.9170(1) | 1.30(3)   |
| 1.76                   | 3.06614(9) | 17.2487(7) | 3.03209(9) | 3.9034(1) | 4.35(3)   |
| 1.96                   | 3.0583(1)  | 17.1992(9) | 3.0224(1)  | 3.8916(3) | 7.12(6)   |
| 1.89                   | 3.0492(2)  | 17.156(1)  | 3.0136(1)  | 3.8770(2) | 10.72(6)  |
| 1.35                   | 3.0411(1)  | 17.1169(7) | 3.00919(8) | 3.8686(2) | 12.90(6)  |
| 1.24                   | 3.0345(1)  | 17.0682(9) | 3.0016(1)  | 3.8574(1) | 15.93(4)  |
| 1.48                   | 3.0305(1)  | 17.0401(9) | 3.0000(1)  | 3.8521(2) | 17.40(5)  |
| 1.35                   | 3.0242(1)  | 17.052(1)  | 2.9958(1)  | 3.8481(2) | 18.51(6)  |
| 1.83                   | 3.0173(3)  | 16.997(2)  | 2.9860(3)  | 3.8347(2) | 22.44(6)  |
| 1.33                   | 3.0103(2)  | 16.990(1)  | 2.9760(2)  | 3.8250(2) | 25.40(6)  |
| 1.16                   | 3.0023(1)  | 16.9199(9) | 2.9704(1)  | 3.8149(2) | 28.61(5)  |
| 1.47                   | 2.9924(1)  | 16.886(1)  | 2.9622(1)  | 3.8026(3) | 32.7(1)   |
| 1.45                   | 2.9848(2)  | 16.855(1)  | 2.9595(1)  | 3.7955(3) | 35.2(1)   |
| 1.37                   | 2.9757(1)  | 16.827(1)  | 2.9470(1)  | 3.7848(2) | 38.95(7)  |
| 1.30                   | 2.9710(2)  | 16.799(1)  | 2.9427(2)  | 3.7787(2) | 41.20(7)  |
| 1.13                   | 2.9641(2)  | 16.754(1)  | 2.9340(1)  | 3.7720(2) | 43.73(7)  |
| 1.18                   | 2.9613(2)  | 16.713(1)  | 2.9276(2)  | 3.7663(2) | 45.93(8)  |
| 1.14                   | 2.9567(2)  | 16.703(1)  | 2.9259(2)  | 3.7605(2) | 48.21(9)  |
| 1.13                   | 2.9512(2)  | 16.679(1)  | 2.9215(20) | 3.7547(2) | 50.56(9)  |
| 1.20                   | 2.9487(2)  | 16.668(1)  | 2.9135(2)  | 3.7467(2) | 53.86(7)  |
| 1.29                   | 2.9479(2)  | 16.665(1)  | 2.9118(2)  | 3.7454(2) | 54.41(7)  |

<sup>a</sup> $R_{wp}$  is the weighted residual associated with each Le Bail refinement.

**Table 2. Refined Lattice Parameters for Mo<sub>1.5</sub>W<sub>0.5</sub>BC and the Associated Pt Pressure Calibrant with Calculated Pressure Values**

| Mo <sub>1.5</sub> W <sub>0.5</sub> BC |              |              |              | Pt           |                |
|---------------------------------------|--------------|--------------|--------------|--------------|----------------|
| $R_{wp}^a$                            | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | <i>a</i> (Å) | <i>P</i> (GPa) |
| 1.61                                  | 3.0790(1)    | 17.3141(9)   | 3.0384(1)    | 3.9183(2)    | 1.04(4)        |
| 1.76                                  | 3.0772(2)    | 17.2838(8)   | 3.0333(1)    | 3.9138(2)    | 2.01(4)        |
| 1.73                                  | 3.0658(1)    | 17.2434(6)   | 3.0244(1)    | 3.9014(2)    | 4.82(5)        |
| 1.44                                  | 3.0606(2)    | 17.212(1)    | 3.0165(2)    | 3.8917(2)    | 7.10(4)        |
| 1.43                                  | 3.0493(2)    | 17.1460(9)   | 3.0106(2)    | 3.8776(2)    | 10.56(4)       |
| 1.51                                  | 3.0382(2)    | 17.110(1)    | 3.0034(2)    | 3.8667(2)    | 13.40(6)       |
| 1.35                                  | 3.0335(2)    | 17.0388(9)   | 2.9970(2)    | 3.8523(2)    | 17.34(5)       |
| 1.51                                  | 3.0247(2)    | 17.028(1)    | 2.9883(2)    | 3.8416(2)    | 20.39(6)       |
| 1.34                                  | 3.0223(2)    | 17.011(1)    | 2.9831(2)    | 3.8365(2)    | 21.91(5)       |
| 1.49                                  | 3.0168(1)    | 16.9365(8)   | 2.9761(1)    | 3.8250(2)    | 25.41(7)       |
| 1.39                                  | 3.0136(2)    | 16.927(1)    | 2.9751(2)    | 3.8221(2)    | 26.33(6)       |
| 1.67                                  | 3.0010(2)    | 16.817(2)    | 2.9664(2)    | 3.8075(3)    | 31.05(9)       |
| 1.68                                  | 3.0010(2)    | 16.812(2)    | 2.9613(2)    | 3.8057(3)    | 31.7(1)        |
| 1.40                                  | 2.9893(2)    | 16.847(2)    | 2.9608(2)    | 3.8004(2)    | 33.45(9)       |
| 1.12                                  | 2.9838(2)    | 16.830(2)    | 2.9504(2)    | 3.7904(2)    | 36.96(6)       |
| 1.14                                  | 2.9804(2)    | 16.829(1)    | 2.9471(2)    | 3.7862(2)    | 38.47(6)       |
| 1.06                                  | 2.9778(2)    | 16.786(2)    | 2.9439(2)    | 3.7799(2)    | 40.76(7)       |
| 1.04                                  | 2.9786(3)    | 16.675(2)    | 2.9367(3)    | 3.7725(2)    | 43.55(7)       |
| 1.07                                  | 2.9650(2)    | 16.680(2)    | 2.9257(2)    | 3.7624(2)    | 47.47(8)       |
| 1.28                                  | 2.9590(2)    | 16.671(2)    | 2.9226(2)    | 3.7534(2)    | 51.08(8)       |
| 1.06                                  | 2.9474(2)    | 16.661(2)    | 2.9191(2)    | 3.7443(2)    | 54.90(7)       |

<sup>a</sup> $R_{wp}$  is the weighted residual associated with each Le Bail refinement.**Table 3. Refined Lattice Parameters for Mo<sub>1.25</sub>W<sub>0.75</sub>BC and the Associated Pt Pressure Calibrant with Calculated Pressure Values**

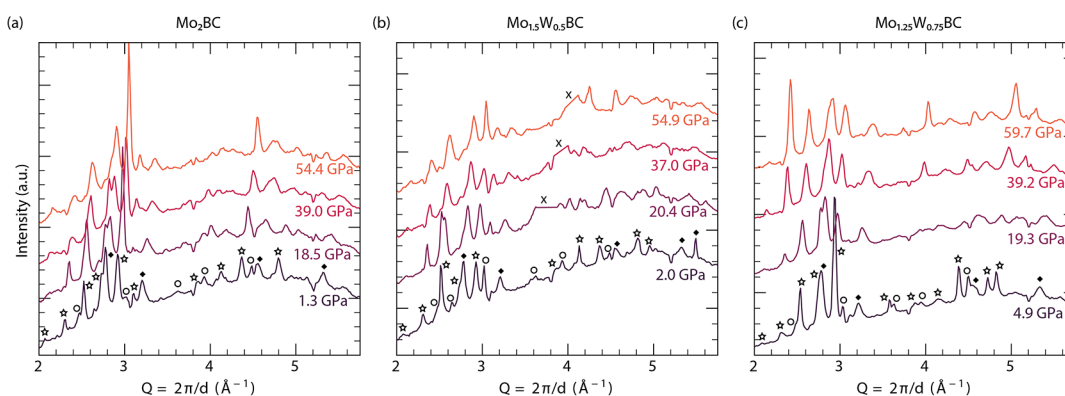
| Mo <sub>1.25</sub> W <sub>0.75</sub> BC |              |              |              | Pt           |                |
|-----------------------------------------|--------------|--------------|--------------|--------------|----------------|
| $R_{wp}^a$                              | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | <i>a</i> (Å) | <i>P</i> (GPa) |
| 1.73                                    | 3.0742(1)    | 17.2984(7)   | 3.0400(1)    | 3.92050(9)   | 0.56(2)        |
| 1.93                                    | 3.06949(8)   | 17.2690(6)   | 3.0374(1)    | 3.9137(1)    | 2.04(2)        |
| 1.78                                    | 3.0585(1)    | 17.2049(7)   | 3.0273(1)    | 3.9008(1)    | 4.94(3)        |
| 2.13                                    | 3.0428(1)    | 17.1623(9)   | 3.0164(1)    | 3.8812(1)    | 9.68(4)        |
| 1.61                                    | 3.0362(1)    | 17.1107(8)   | 3.0070(1)    | 3.8704(1)    | 12.43(4)       |
| 1.84                                    | 3.0342(1)    | 17.0933(7)   | 3.00377(8)   | 3.8644(1)    | 14.03(3)       |
| 1.63                                    | 3.0263(2)    | 17.075(1)    | 2.9949(1)    | 3.8552(1)    | 16.54(4)       |
| 2.09                                    | 3.0193(2)    | 17.050(1)    | 2.9918(2)    | 3.8452(2)    | 19.35(4)       |
| 1.68                                    | 3.0227(2)    | 16.985(1)    | 2.9886(1)    | 3.8390(1)    | 21.16(4)       |
| 1.94                                    | 3.0014(2)    | 16.969(1)    | 2.9699(1)    | 3.8224(2)    | 26.23(6)       |
| 1.65                                    | 2.9988(2)    | 16.893(1)    | 2.9665(2)    | 3.8160(2)    | 28.28(5)       |
| 1.50                                    | 2.9894(2)    | 16.870(1)    | 2.9555(1)    | 3.8027(1)    | 32.67(5)       |
| 2.63                                    | 2.9836(3)    | 16.829(2)    | 2.9494(3)    | 3.7922(2)    | 36.31(9)       |
| 1.49                                    | 2.9777(1)    | 16.754(1)    | 2.9404(1)    | 3.7841(1)    | 39.23(4)       |
| 1.47                                    | 2.9721(1)    | 16.736(1)    | 2.9384(1)    | 3.7796(1)    | 40.88(5)       |
| 1.29                                    | 2.9643(1)    | 16.6907(9)   | 2.9319(1)    | 3.7712(1)    | 44.06(4)       |
| 1.42                                    | 2.9586(1)    | 16.659(1)    | 2.9246(1)    | 3.7632(1)    | 47.17(5)       |
| 1.40                                    | 2.9496(1)    | 16.608(1)    | 2.9163(1)    | 3.7501(1)    | 52.45(5)       |
| 1.38                                    | 2.9453(1)    | 16.589(1)    | 2.9104(1)    | 3.7442(1)    | 54.93(5)       |
| 1.50                                    | 2.9396(1)    | 16.545(1)    | 2.9049(1)    | 3.7360(1)    | 58.47(6)       |
| 1.62                                    | 2.9357(1)    | 16.537(1)    | 2.9000(1)    | 3.7333(2)    | 59.66(7)       |

<sup>a</sup> $R_{wp}$  is the weighted residual associated with each Le Bail refinement.

arc melted samples to a fine powder, mixing in 5% ruby powder and 10% platinum powder as pressure calibrants.<sup>24</sup> The finest particles were isolated from the bulk powder through solvent suspension in methanol. This process was repeated on the isolated material to achieve an even finer particle size. Sample/Pt mixtures were loaded into a 45–60 μm diameter sample chamber that was laser milled into stainless steel gasket material after preindention to a thickness of ~40

μm from an initial thickness of 250 μm. To achieve near-hydrostatic conditions, sample mixtures were gas loaded into the sample chamber with a neon pressure medium. High-pressure conditions were achieved using a symmetric DAC with 200 μm diameter flat culet diamond anvils.

Facilities of the High Pressure Collaborative Access Team (HPCAT) at beamline sector 16-ID-B of the Advanced Photon



**Figure 2.** Several representative synchrotron diffraction spectra collected upon hydrostatic compression of (a)  $\text{Mo}_2\text{BC}$ , (b)  $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$ , and (c)  $\text{Mo}_{1.25}\text{W}_{0.75}\text{BC}$ . Prominent peaks associated with platinum (◆), ruby (○), and each borocarbide (☆) are identified in the low-pressure diffraction patterns. The broad feature observed at elevated pressures in (b)  $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$ , marked by (x), is likely attributed to the neon pressure medium.

Source were used to perform the synchrotron experiments. The  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  samples were incrementally compressed to  $\sim 55$ – $60$  GPa in steps of 1–5 GPa at ambient temperature. At each step, monochromatic X-rays ( $\lambda = 0.4066$  Å) and a Pilatus detector were used to collect angle-dispersive diffraction spectra in axial geometry. X-ray energy was  $\sim 30.5$  keV, and the beam was focused to  $5 \times 4$   $\mu\text{m}$ . A cerium dioxide standard was used to calibrate sample-to-detector distance (209.7 mm), detector tilt, and detector rotation. Collected 2D diffraction images were converted from polar coordinates to Cartesian coordinates using FIT2D.<sup>25</sup> Lattice parameters were determined from the diffraction data using the Le Bail method as implemented in the MAUD (Materials Analysis Using Diffraction) software package.<sup>26</sup> Because near-hydrostatic conditions were maintained, lattice strain was not refined. An isothermal, third-order Birch–Murnaghan EOS (eq 1) was fit to the relative cell volume versus pressure curves using EOSFit software to determine  $K_0$  and the first pressure derivative of the bulk modulus,  $K'_0$ .<sup>27</sup>

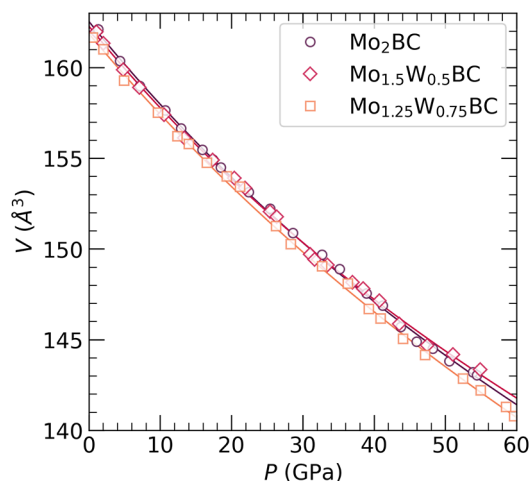
$$P(V) = \frac{3K_0}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left[ 1 + \frac{3}{4}(K'_0 - 4) \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right] \quad (1)$$

## RESULTS AND DISCUSSION

To determine  $K_0$  values of three  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions ( $x = 0, 0.5, 0.75$ ), synchrotron diffraction patterns were collected upon hydrostatic DAC compression. The diffraction data were evaluated using MAUD software, refining lattice parameters of both the borocarbitides and internal platinum pressure calibrant to monitor pressure.<sup>24,26</sup>  $\text{Mo}_2\text{BC}$ ,  $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$ , and  $\text{Mo}_{1.25}\text{W}_{0.75}\text{BC}$  were compressed to  $\sim 54$  GPa,  $\sim 55$  GPa, and  $\sim 60$  GPa, respectively, as determined by the platinum EOS. Refined lattice parameters, associated error, and calculated pressure values are presented in Tables 1–3. As hydrostatic conditions are necessary to reliably calculate bulk modulus, neon was selected as the pressure transmitting medium because it has been shown to maintain quasi-hydrostatic conditions to pressures upward of 50 GPa.<sup>28</sup> Raw 2-D diffraction spectra are presented in the Supporting Information (Figure S1) to demonstrate maintained hydrostaticity of the three  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions evaluated. If present, lattice strain would be revealed through sinusoidal variations in peak position, so no significant lattice strain is observed upon compression to  $P > 50$  GPa. Figure 2 illustrates select, representative diffraction patterns collected for each  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solution. Peaks shift to higher  $Q$ -space values with increasing pressure, indicating compression of the

crystal structure. In the collected spectra, observed peaks are indexed to either the orthorhombic borocarbide phase or to the platinum or ruby internal pressure calibrants, with no indication of phase transformations across the entire pressure range. Prominent platinum, ruby, and borocarbide peaks are labeled. However, when the high pressure diffraction data for  $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$  is examined, a broad feature develops between  $Q = 3.6$  and  $4.0$   $\text{\AA}^{-1}$ . This feature overlaps with several minor diffraction peaks associated with the sample and pressure calibrants but can likely be attributed to diffraction of the neon pressure medium. To illustrate all collected diffraction data for each  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solution, Supporting Information Figure S2 presents a heatmap of peak intensity with increasing pressure.

The refined unit cell volume ( $V$ ) is plotted as a function of calculated pressure for each solid solution in Figure 3, while a third-order Birch–Murnaghan EOS (eq 1) is fit to each data set to determine  $V_0$ ,  $K_0$ , and  $K'_0$ .<sup>27</sup> Unit cell volume was plotted rather than relative volume ( $V/V_0$ ) to help distinguish the three data sets. Table 4 presents the experimentally determined  $V_0$ ,  $K_0$ , and  $K'_0$  for each of the three solid solutions, as well as values for a  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$  composition from a previous work



**Figure 3.** Unit cell volume is plotted against pressure for each of the three  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions, and a third-order Birch–Murnaghan EOS is fit to each data set. Error bars are smaller than the marker size in each case.

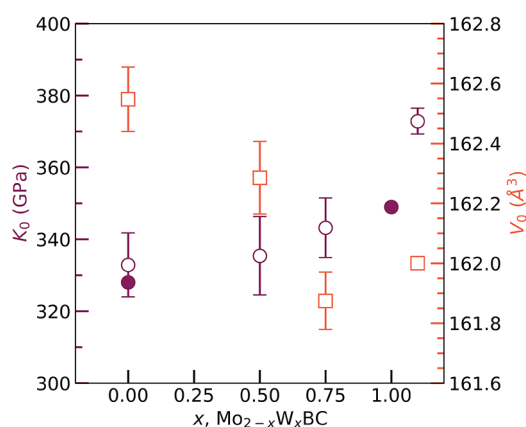
**Table 4. Experimentally Determined  $V_0$ ,  $K_0$ , and  $K'_0$  for  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  Solid Solutions<sup>a</sup>**

| composition                                            | third-order B-M EOS     |             |        | DFT <sup>18</sup> | <i>ab initio</i> <sup>20</sup> |
|--------------------------------------------------------|-------------------------|-------------|--------|-------------------|--------------------------------|
|                                                        | $V_0$ (Å <sup>3</sup> ) | $K_0$ (GPa) | $K'_0$ | $K_0$ (GPa)       | $K_0$ (GPa)                    |
| $\text{Mo}_2\text{BC}$                                 | 162.5(1)                | 333(9)      | 3.7(4) | 328               | 324                            |
| $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$               | 162.3(1)                | 335(11)     | 4.1(5) |                   |                                |
| $\text{Mo}_{1.25}\text{W}_{0.75}\text{BC}$             | 161.9(1)                | 343(8)      | 3.2(3) |                   |                                |
| $\text{MoWBC}$                                         |                         |             |        | 349               |                                |
| $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$ <sup>23</sup> | 162.000(3)              | 373(4)      | 2.3(2) |                   |                                |

<sup>a</sup>Experimental results from a previous work are included.<sup>23</sup> DFT and *ab initio* calculated values for  $\text{Mo}_2\text{BC}$  and  $\text{MoWBC}$  are also presented for comparison.<sup>18,20</sup>

and density functional theory (DFT) and *ab initio* calculated values for  $\text{MoWBC}$  and  $\text{Mo}_2\text{BC}$  from other sources.<sup>18,20,23</sup>

Figure 4 portrays the observed  $V_0$  and  $K_0$  as a function of W content.



**Figure 4.**  $K_0$  and  $V_0$  plotted against  $x$  in  $\text{Mo}_{2-x}\text{W}_x\text{BC}$ . Circular, purple markers are associated with  $K_0$ , while square, orange markers are associated with  $V_0$ . The  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$  results are from a previous work.<sup>23</sup> Experimentally determined values are plotted as open markers, while previous DFT calculated  $K_0$  values are plotted as solid markers for comparison.<sup>18</sup>

For the experimentally evaluated  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions,  $K_0$  generally appears to correlate with increasing W content and decreasing Mo content, from  $K_0 = 333(9)$  GPa for  $\text{Mo}_2\text{BC}$  to  $K_0 = 373(4)$  GPa for  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$ .<sup>23</sup> Admittedly, though  $K_0$  seems to express a slightly increasing trend for  $\text{Mo}_2\text{BC}$ ,  $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$ , and  $\text{Mo}_{1.25}\text{W}_{0.75}\text{BC}$ , experimental uncertainty does not allow this claim to be entirely supported. However, alongside the aforementioned bulk modulus for  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$  and previously reported DFT results, the trend is substantiated. DFT and *ab initio* calculated  $K_0$  values for  $\text{Mo}_2\text{BC}$ , reported as  $K_0 = 324$  GPa and  $K_0 = 328$  GPa by Emmerlich et al. and Mansouri Tehrani et al., respectively, are in good agreement with the experimentally determined value reported here.<sup>18,20</sup> Mansouri Tehrani et al. also report  $K_0 = 349$  GPa for  $\text{MoWBC}$  through DFT calculations. These findings indicate that bulk compressibility of the  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  structures, particularly the tungsten-rich compositions, are comparable to values reported for  $\text{WB}_4$  ( $K_0 = 369(9)$  GPa and  $K'_0 = 1.2(5)$ ).<sup>29</sup> Additionally, the calculated  $V_0$  of  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  generally decreases as W content increases, in agreement with

X-ray diffraction results reported previously, and can be explained by shorter, stronger bonding among the TMs.<sup>18</sup> Reduced crystal volume also correlates to increased valence electron density, and therefore incompressibility, supporting the observed trend in  $K_0$  for  $\text{Mo}_2\text{BC}$ ,  $\text{Mo}_{1.5}\text{W}_{0.5}\text{BC}$ , and  $\text{Mo}_{1.25}\text{W}_{0.75}\text{BC}$ . Conversely, zero-pressure unit cell volume of  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$  was reported to be  $V_0 = 162.000(3)$  Å<sup>3</sup>, while  $\text{Mo}_{1.25}\text{W}_{0.75}\text{BC}$  is reported here as  $V_0 = 161.9(1)$  Å<sup>3</sup>.<sup>23</sup> It is possible that experimental uncertainty is responsible for this apparent deviation from the aforementioned trend. Nonetheless, these results demonstrate the capacity of TM substitution to manipulate atomic size effects and valence electron density to tailor the mechanical response.

In addition to the exceptional bulk moduli of the  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  system, DFT calculated shear moduli of  $\text{Mo}_2\text{BC}$  ( $G = 189$  GPa) and  $\text{MoWBC}$  ( $G = 202$  GPa) are comparable to those of other high-hardness materials.<sup>18,21,30</sup> The elevated shear moduli indicate a limited susceptibility to slip and general resistance to plastic deformation, and alongside the reported bulk moduli, rationalize the high hardness and moderate ductility. However, the anisotropic crystal structure (Figure 1) suggests a nonuniform mechanical response. Therefore, understanding the elastic moduli, hardness, and ductility in the context of anisotropic lattice strain and texture development when exposed to nonhydrostatic stresses can inform future efforts to implement  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions in applications requiring wear-resistance. Previous nonhydrostatic compression experiments on  $\text{Mo}_{0.9}\text{W}_{1.1}\text{BC}$  investigated anisotropic deformation behavior and found that the (002) and (200) planes parallel to the long  $b$ -axis support the greatest differential strain.<sup>31</sup> These planes are orthogonal to the covalently bonded boron chains, which likely provide additional elastic support and decrease the susceptibility to slip. Lattice preferred orientation was demonstrated along planes parallel to the covalent chains, suggesting that dislocation glide occurs in directions that do not require the breaking of B–B bonds. Furthermore, Mansouri Tehrani et al. used stress–strain calculations to investigate the anisotropic, nonlinear elastic behavior of  $\text{Mo}_2\text{BC}$  and observed tensile strain stiffening along the [001] direction.<sup>32</sup> The observed stiffening was attributed to the formation of an electronic pseudogap within the density of state and the dimerization of the boron–boron chains, delaying shear failure and enhancing ultimate strength and strain. Additionally, the (111)[ $\bar{1}\bar{1}2$ ] was identified as the softest shear plane, contributing to the ductility of the structure. Because the  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions are isostructural, it is anticipated that the deformation mechanisms are similar across this system.

## CONCLUSIONS

The  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  system demonstrates the potential to optimize hardness, ductility, and sustainability in synthetically accessible inorganic materials for applications requiring wear-resistant, superhard materials. In this work, bulk compressibility of  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions, where  $x = 0, 0.5$ , and  $0.75$ , was evaluated through *in situ* hydrostatic, high-pressure synchrotron diffraction experiments to  $\sim 54$  GPa,  $\sim 55$  GPa, and  $\sim 60$  GPa, respectively. The calculated Birch–Murnaghan EOS values for each composition demonstrate an increase in  $K_0$  with rising W content and are in good agreement with previous computational studies. Furthermore,  $V_0$  decreases as Mo is substituted by W, corresponding to the increase in valence electron density, hardness, and  $K_0$ . Experimental

determination of trends in  $K_0$  within  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions can inform future computational and experimental design endeavors in the search for environmentally sustainable materials with superb mechanical response.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.1c03501>.

Raw 2-D diffraction spectra collected at low and high pressures for each of the three  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions, where  $x = 0, 0.5$ , and  $0.75$ , depicting the lack of lattice strain observed upon compression; diffraction spectra for the three  $\text{Mo}_{2-x}\text{W}_x\text{BC}$  solid solutions presented as intensity maps, depicting a shift in  $Q$ -space upon compression to  $P > 50$  GPa (PDF)

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### Notes

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